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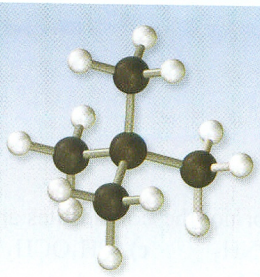


Organic Compounds: A First Look

CHAPTER 2

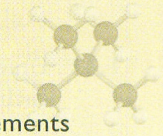
Now that you have refreshed your basic understanding of bonding, you are ready to examine organic compounds in more detail. The purpose of this chapter is to provide more experience with simple organic molecules. You will learn about how their atoms are connected (the structure of the molecule) and how their structures affect some of their properties.

The chapter begins with a description of how atoms usually bond in molecules, including a discussion of bond lengths and bond strengths. Next, structural formulas, which show how the atoms of a molecule are connected, are discussed in detail. Structural formulas are very important in organic chemistry because atoms for most molecular formulas can be assembled in many different ways, resulting in the possibility of isomers. Therefore, a structural formula for a molecule is needed to specify a particular compound. A useful aid in drawing structural formulas, called the degree of unsaturation, is presented. Then we learn how examining the structure of a compound enables us to estimate the physical properties of that compound. It is possible to predict whether a compound is likely to be a solid, a liquid, or a gas at room temperature; whether it is likely to be water soluble; and so forth. Finally, an extremely important organizing concept, the functional group, is introduced.

2.1 Common Bonding Situations

In Chapter 1 we learned that molecules that satisfy the octet rule are likely to be stable. Furthermore, we learned that the presence of formal charges in a molecule is often a destabilizing factor. The common ways in which atoms are bonded can be understood by using these two criteria.

Mastering Organic Chemistry



- Recognizing Stable Bonding Arrangements
- Understanding the Trends in Bond Strengths and Bond Lengths
- Drawing Constitutional Isomers
- Calculating and Using the Degree of Unsaturation
- Using Line Structures, Condensed Structures, and Skeletal Structures
- Understanding How the Attractive Forces between Molecules Affect Melting Points, Boiling Points, and Solubilities
- Recognizing Functional Groups

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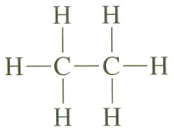
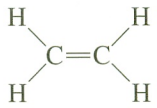
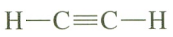
(a) Hydrogen almost always has one bond. Exceptions are very rare.

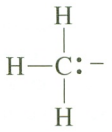
(b) Carbon in its most stable form has four bonds. These may be single, double, or triple bonds. These are by far the most common bonding situations for carbon.





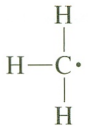


Carbon is sometimes encountered with only three bonds and a negative charge. Such **carbanions** are less stable than the compounds above, but they are still important.

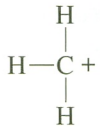


A carbanion

Carbon **radicals**, with only seven electrons in the valence shell for carbon, and **carbocations**, with only six electrons and a positive charge on the carbon, do not satisfy the octet rule and are quite unstable. These species are only encountered as highly reactive, transient intermediates in certain chemical reactions.



A radical



A carbocation

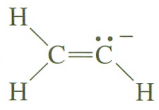
Figure 2.1
BONDING ARRANGEMENTS FOR (a) HYDROGEN AND (b) CARBON.

Thus, carbon usually forms four bonds. Any other arrangement either does not satisfy the octet rule or has a charge on the carbon. However, carbon is occasionally encountered in one of these less stable bonding arrangements. Both the common and more unusual bonding situations for various atoms are shown in Figures 2.1, 2.2, and 2.3.

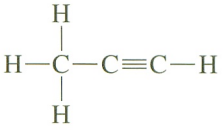
PROBLEM 2.1

Discuss the stability of each of these species based on the octet rule and formal charges:

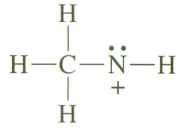
a)



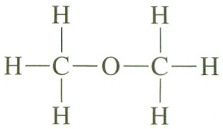
b)



c)



d)



e)

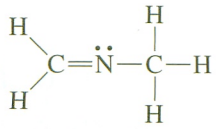
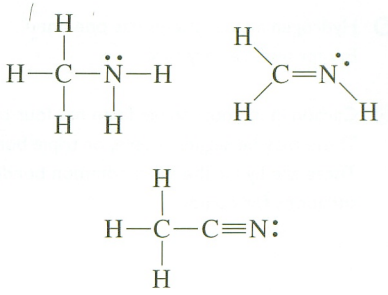


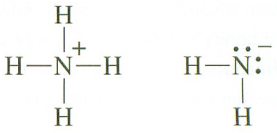
Figure 2.2

BONDING ARRANGEMENTS FOR (a) NITROGEN, (b) OXYGEN, AND THE (c) HALOGENS.

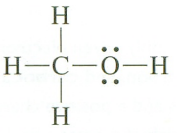
(a) Nitrogen usually has one unshared pair of electrons and three bonds. The bonds may be single, double, or triple.

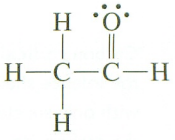


Nitrogen is also encountered with four bonds and a positive charge or with two bonds, two unshared pairs of electrons, and a negative charge. Because both of these species satisfy the octet rule, they are relatively common.



(b) Oxygen usually has two bonds and two unshared pairs of electrons. The bonds may be single or double.





Oxygen with one bond, three pairs of electrons, and a negative charge or with three bonds, one unshared pair of electrons, and a positive charge is also relatively common.

(c) The halogens usually have one bond and three unshared pairs of electrons. They are also found as stable negative ions. In addition, Cl, Br, and I can have more than eight electrons in their valence shells.

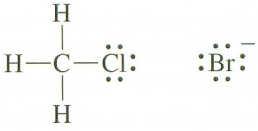
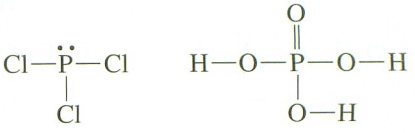


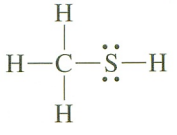
Figure 2.3

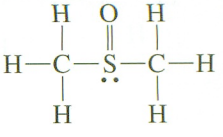
BONDING ARRANGEMENTS FOR (a) PHOSPHORUS AND (b) SULFUR.

(a) Because phosphorus is beneath nitrogen in the periodic table, it has similar bonding tendencies. Thus, phosphorus often has three bonds and one unshared pair of electrons. However, because phosphorus is in the third row of the periodic table, it can have more than eight electrons in its valence shell.



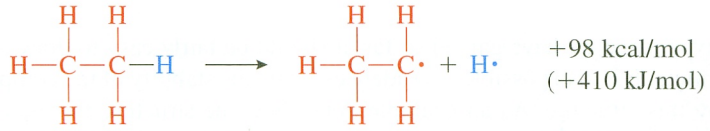
(b) Sulfur is beneath oxygen in the periodic table. Therefore, it often has two bonds and two unshared pairs of electrons. Sulfur can also have more than eight electrons in its valence shell.





2.2 Bond Strengths and Bond Lengths

In the common bonding situations illustrated in Figures 2.1, 2.2, and 2.3, the bonds are stable. This implies that a considerable amount of energy must be added to a compound to break one of these bonds. One measure of the strength of a bond is the **bond dissociation energy.** This is defined as the amount of energy that must be added in the gas phase to break the bond in a homolytic fashion, that is, breaking the bond in a symmetrical manner, with one electron remaining with each of the atoms. For example, homolytic cleavage of one of the carbon–hydrogen bonds of ethane, as shown next, requires an input of 98 kcal/mol (410 kJ/mol) of energy. Therefore, the bond dissociation energy for one C—H bond in ethane is 98 kcal/mol (410 kJ/mol).



The C—H bond dissociation energy is not the same for all compounds. It depends on the other bonds to the carbon also. For example, the C—H bond dissociation energy for methane, CH_4, is 104 kcal/mol (435 kJ/mol), compared to 98 kcal/mol (410 kJ/mol) for ethane. Of course, other bond dissociation energies also depend on the other bonds to the atoms involved.

Table 2.1 lists typical bond dissociation energies for many of the bonds of interest. Table 2.2 lists approximate bond lengths for these same bonds. Rather than memorizing the numbers, let's see what trends can be discerned from this information.

1. A correlation exists between bond length and bond strength: stronger bonds tend to be shorter.
2. Bonds between H and the second-row elements C, N, and O are all strong—close to 100 kcal/mol (418 kJ/mol). The bond lengths are about 1 Å (1 Å = 10^{-10} m = 100 pm).
3. Bonds between C and the other second-row elements are also reasonably strong—in the vicinity of 70 to 80 kcal/mol (290–335 kJ/mol). The bond lengths are all near 1.5 Å. For these multivalent atoms, note that only carbon forms strong bonds to itself and to the other atoms. For example, even in situations in which the octet rule is satisfied, the O—O bond dissociation energy is only 34 kcal/mol (142 kJ/mol), and that for N—O is only 39 kcal/mol (163 kJ/mol). These bonds are weaker than C—C bonds because of repulsion between the unshared pairs of electrons on the bonded atoms. For this reason, only chains of bonded carbons are commonly encountered.
4. The carbon–halogen bonds become weaker and longer as the atomic number of the halogen increases. This is also true for bonds involving other atoms from the third and subsequent periods of the periodic table. For example, the Si—Si bond is much weaker than the C—C bond.
5. Double and triple bonds are stronger and shorter than single bonds. However, note that a C—C double bond is not twice as strong as a C—C single bond, nor is a triple bond three times as strong. On the other hand, a C—O double bond is very strong, more than twice as strong as a C—O single bond. Therefore, the C—O double bond is a common and important bond.

Chapter 3 discusses the reasons behind these trends.

Table 2.1 *Typical* Bond Dissociation Energies

Bond	Bond Dissociation Energy
C—H	98 (410)
N—H	92 (385)
O—H	109 (456)
C—C	81 (339)
C—N	66 (276)
C—O	79 (330)
C—F	116 (485)
C—Cl	79 (330)
C—Br	66 (276)
C—I	52 (217)
C=C	145 (606)
C≡C	198 (828)
C=O	173 (723)
C≡N	204 (854)

Values are in units of kcal/mol. Values in parentheses are in units of kJ/mol.

Table 2.2 Approximate Bond Lengths

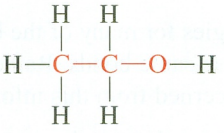
Bond	Bond Length
C—H	1.10
N—H	1.00
O—H	1.00
C—C	1.54
C—N	1.47
C—O	1.41
C—F	1.38
C—Cl	1.78
C—Br	1.94
C—I	2.14
C=C	1.34
C≡C	1.20
C=O	1.20
C≡N	1.16

Values are in units of angstroms (1 Å = 10^{-10} m).

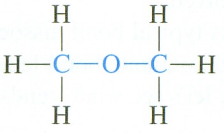
Most organic compounds are based primarily on covalent bonds to carbon. These carbons are bonded to other carbons in chains or rings. They may also be bonded to hydrogen. In addition, compounds with C bonded to O and N (these may have bonds to H) and to the halogens (especially Cl and Br) are common. Compounds involving S and P or the other elements are stable but less common. Carbon may be doubly bonded to C, N, or O or triply bonded to C or N. Although these are neither the only stable bonds nor the only important bonds, they are the ones that are encountered most often.

2.3 Constitutional Isomers

With the experience we have gained so far, it should be fairly easy to draw a structure for any formula. It is also possible to crudely estimate the stability of the compound represented by this structure. As an example, let's show the structure for the compound with the formula C_2H_6O. We quickly discover that there are two ways to assemble these atoms, depending on whether we start with a C—C—O or a C—O—C arrangement of the nonhydrogen atoms.



Ethanol
(ethyl alcohol)



Dimethyl ether

Which of these two structures is correct? Both of them satisfy the octet rule and neither has formal charges, so both are predicted to be of comparable stability. On the basis of what we have discussed so far, we cannot predict which is more stable. In fact, both of these compounds are quite stable and can be "put in a bottle." But they are different compounds. Ethyl alcohol is the "alcohol" found in beverages. It is a liquid at room temperature. In contrast, dimethyl ether is a gas at room temperature and is quite poisonous. As was mentioned in Section 1.7, compounds such as these, with the same molecular formula but different arrangements of bonded atoms (different structures or different connectivities), are called **constitutional isomers** (or structural isomers). Constitutional isomerism is very common in organic compounds. This is another reason why it is necessary to show the structure of the compound under discussion rather than just the molecular formula.

As the number of atoms in a formula increases, the number of possible constitutional isomers increases dramatically. As an illustration, consider the series of **hydrocarbons** (compounds made up of only carbon and hydrogen) shown in Table 2.3. Although there is only one compound with the formula CH_4, there are 75 constitutional isomers with the formula $C_{10}H_{22}$ (all 75 have been prepared in the lab and identified) and more than 4 billion with the formula $C_{30}H_{62}$!

A general method for calculating the number of isomers of a given molecular formula has not yet been developed. The problem is just too complex. However, several

Table 2.3 The Number of Constitutional Isomers for a Series of Hydrocarbons

Formula	Number of Constitutional Isomers
CH_4	1
C_2H_6	1
C_3H_8	1
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{20}H_{42}$	366,319
$C_{30}H_{62}$	4,111,846,763

methods have been developed that work for specific cases. One of these was used to determine the number of isomers with the formula $C_{30}H_{62}$. More recently, a type of mathematics called graph theory has been applied with some success to some types of molecular formulas. Nevertheless, a general solution has remained elusive. So we will have to rely on drawing all of the different structures if we want to determine the number of isomers of a particular formula. Obviously, this can be done only for simple cases.

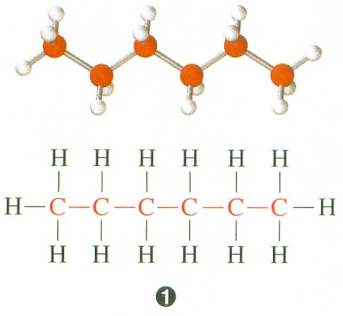
How many of the virtually limitless number of organic compounds are known? The organization Chemical Abstracts Service (CAS) has the task of reviewing every article in every chemical journal that is published and tabulating all of the compounds that have been characterized and reported in these articles. Most of these compounds are organic. The CAS registry listed more than 22 million compounds as of 2003.

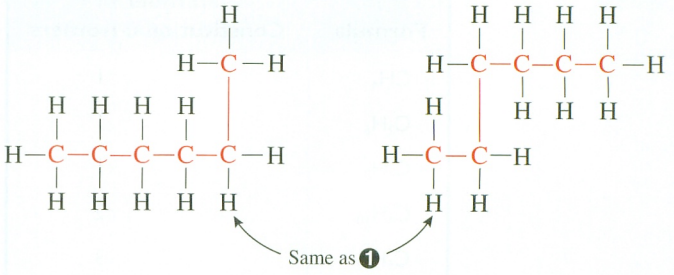
Beginning students usually have difficulty drawing all the isomers for a particular formula without omitting or duplicating any. However, we can do this for simpler examples if a systematic approach is used. The process is illustrated in Figure 2.4 for C_6H_{14}. It is important to recognize that these structures show only the connectivity of the isomer; they do not show the shapes of the molecules. (Chapter 6 deals with that.) No matter how an individual structure is twisted or turned, as long as the connectivity remains the same, the structure represents the same isomer.

PROBLEM 2.2

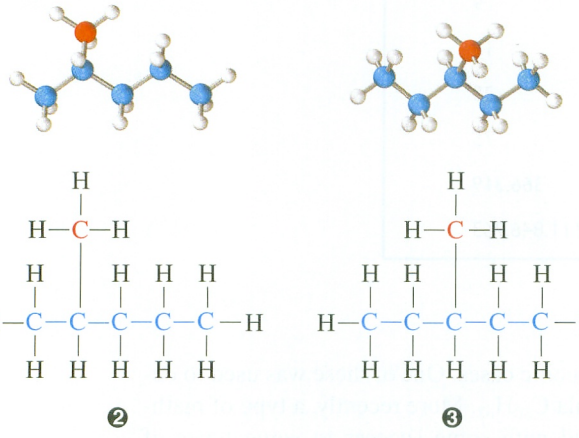
Draw the three constitutional isomers that have the formula C_5H_{12}.

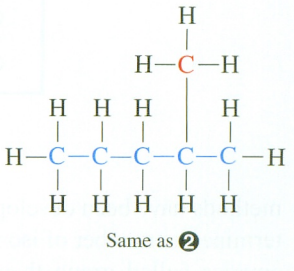
For the first isomer, start with a straight chain of six carbons. Then add the hydrogens to produce isomer ❶. Note that this isomer has a continuous chain of C's. It does not make any difference whether the C's are drawn straight or bent, since we are not trying to show the shape of the molecule. The drawings below are other ways to represent isomer ❶.





For the second isomer, start with a chain of five C's. Add the remaining C to any of the inside C's. (If the remaining C is added to either end C, isomer ❶ would be produced.) There are two different ways to do this, resulting in isomers ❷ and ❸. Note that the final structure below is just isomer ❷ turned around.





The total is five isomers. To get the final two, begin with a chain of four C's. Add the two remaining C's to the middle C's, as shown in isomers ❹ and ❺. Any other arrangement will produce one of these five isomers. For example, if both the remaining C's are added as a two-carbon chain to one of the middle C's, a bent version of isomer ❸ is produced.

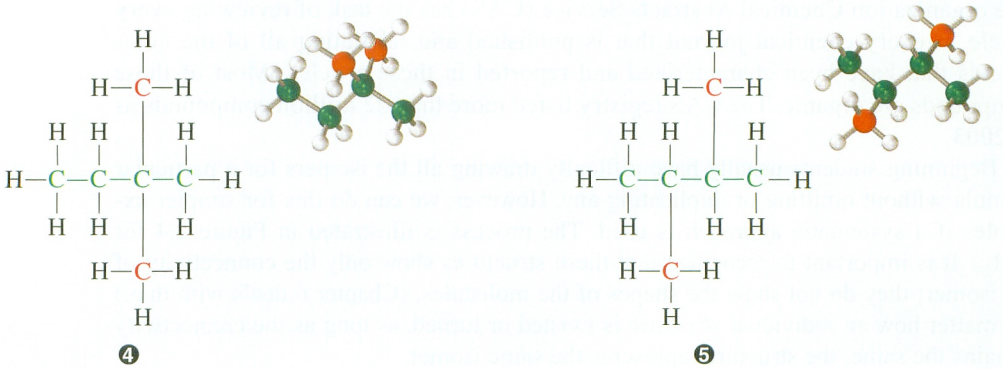


Figure 2.4

CONSTITUTIONAL ISOMERS FOR C_6H_{14}.

PRACTICE PROBLEM 2.1

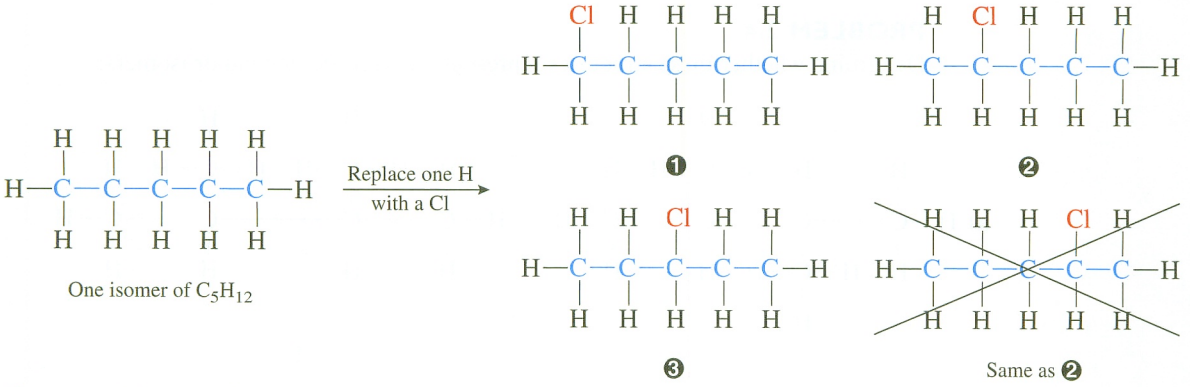
There are eight constitutional isomers that have the formula $C_5H_{11}Cl$. Show a structure for each of them.

Strategy

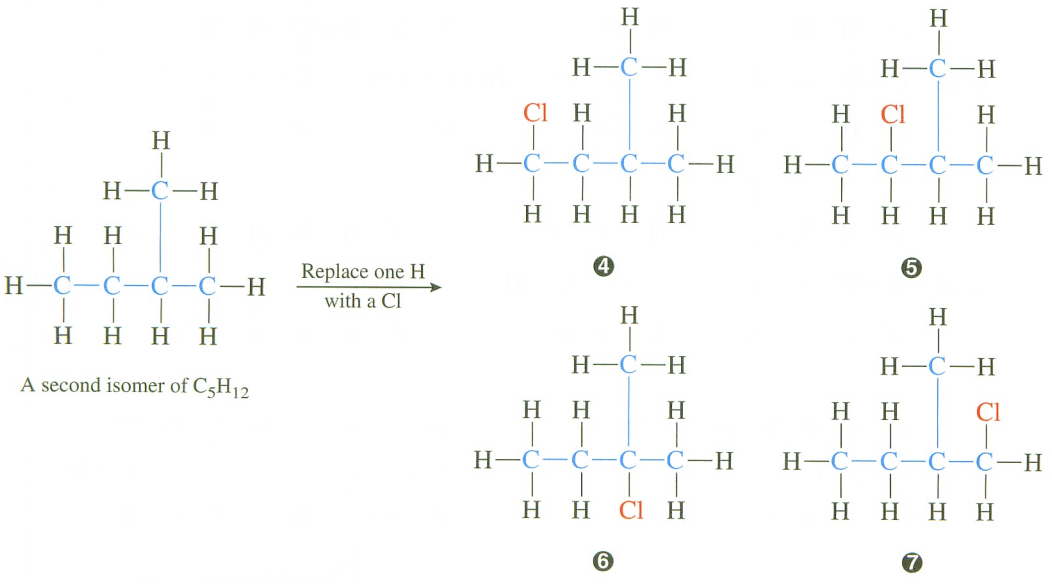
In problems like this one, it is important to be as systematic as possible or you will never get all of the isomers. It is helpful to recognize that Cl has a valence of 1, just like H. Therefore, $C_5H_{11}Cl$ can be viewed as resulting from replacing one H of C_5H_{12} with a Cl. C_5H_{12} has three isomers (see problem 2.2). Each of these will give rise to a different set of $C_5H_{11}Cl$ isomers. So start with each isomer of C_5H_{12} and replace each different H with a Cl.

Solution

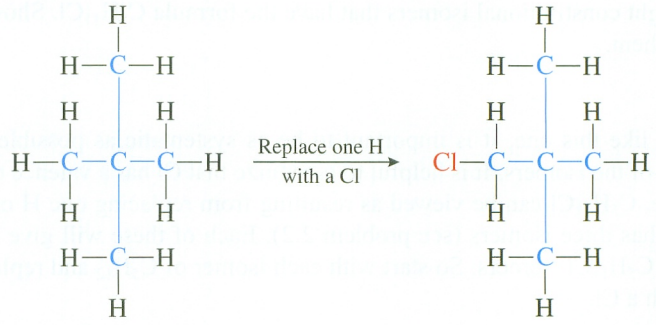
Start with the straight-chain isomer of C_5H_{12}. This compound has three different types of hydrogens, so three isomers of $C_5H_{11}Cl$ result by replacing these hydrogens with chlorine.



The second isomer of C_5H_{12} gives four isomers of $C_5H_{11}Cl$:



The third isomer of C_5H_{12} is very symmetrical. All of its hydrogens are identical, so it gives only one isomer of $C_5H_{11}Cl$. We get eight isomers in total.



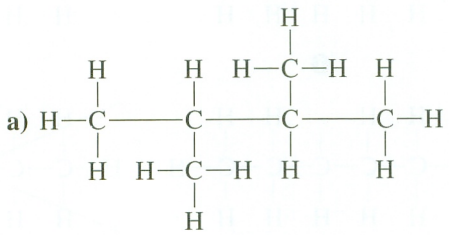
The third isomer of C_5H_{12} ❽

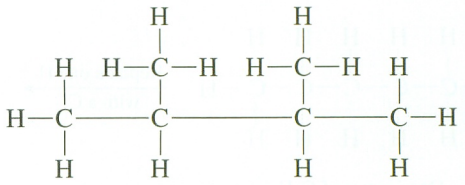
PROBLEM 2.3

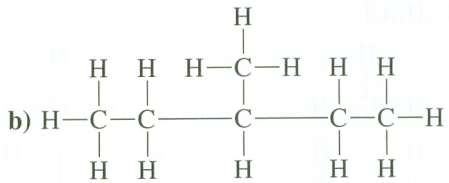
The formula $C_4H_{10}O$ results in seven isomers. See how many you can draw.

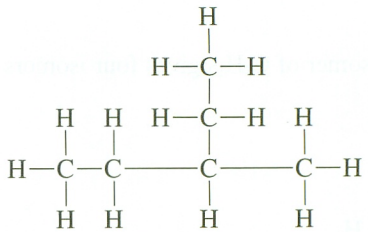
PROBLEM 2.4

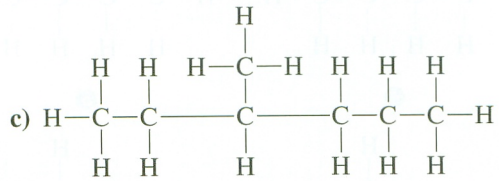
Determine whether these structures represent the same compound or isomers:

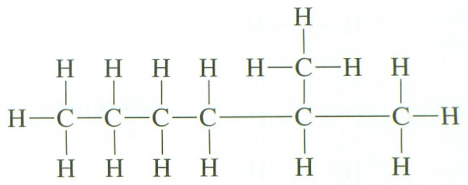


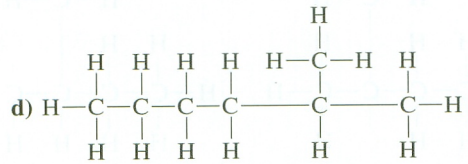


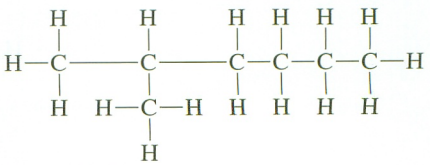










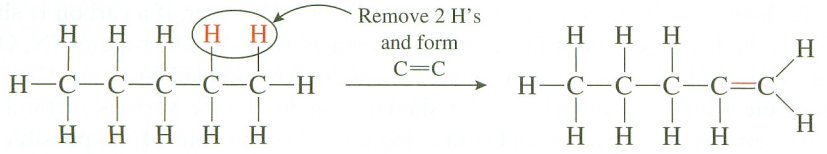


2.4 Degree of Unsaturation

The task of drawing isomers for a particular formula can be made easier by comparing the number of hydrogens with the number of carbons in the formula. Such a comparison allows the calculation of the **degree of unsaturation,** which furnishes useful information about possible structures that will fit the formula (such as whether double bonds can be present) and provides a starting point for drawing isomers.

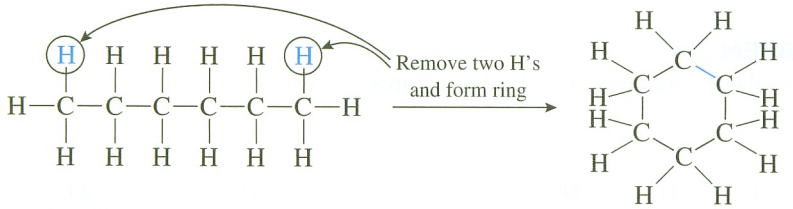
The isomers shown in Figure 2.4 have the maximum number of hydrogens possible for a compound with six carbons. The maximum number of H's can easily be calculated from the number of C's present. To see how the formula arises, consider a straight, or linear, chain of some number of C's. Each C has two H's bonded to it, with the exception that the two end C's have one additional H, because they are bonded to only one C. Therefore, for n carbons, the maximum number of hydrogens is $2n + 2$. The general formula for a hydrocarbon with the maximum number of hydrogens is C_nH_{2n+2}. As an example, C_5H_{12} has the maximum number of H's for 5 C's [$2(5) + 2 = 12$].

Now let's see what happens to the number of hydrogens in a compound if a double bond is present. To form a double bond, a hydrogen must be removed from each of two adjacent carbons. Therefore, a compound with one double bond has two fewer H's than the maximum.



C_5H_{12} C_5H_{10}

Similarly, to form a ring from a chain of carbons, one H must be removed from both end C's so that they can be bonded together. A compound with a ring also has two fewer H's than the maximum number.



C_6H_{14} C_6H_{12}

Any compound whose formula has *two* hydrogens less than the maximum number possible ($2n + 2$) must contain *one* double bond or *one* ring. The total number of multiple bonds plus rings is called the **degree of unsaturation (DU)** and is equal to 1 for this case. The DU of a compound can be calculated by using the following formula:

$$\text{DU} = \frac{(\text{Maximum possible H's}) - (\text{Actual H's})}{2}$$

For a hydrocarbon with the formula C_nH_x the degree of unsaturation is

$$\text{DU} = \frac{(2n + 2) - x}{2}$$

where

n = actual C's present

x = actual H's present

The DU is very useful when drawing isomers. Let's look at a simple example. Suppose we are asked to draw the constitutional isomers with the formula C_5H_{10}. The DU for C_5H_{10} is $[(2(5) + 2) - 10]/2 = 1$. Therefore, this compound must have one double bond or one ring. Any compound that has five C's and one double bond or one ring will fit the formula. Although C_5H_{12} has only three isomers, having two fewer H's actually increases the number of isomers, because there is now a double bond or a ring to vary.

As structures become more complex, drawing them as a **line** or **Kekulé structure,** in which each bond is shown as a line, becomes more time consuming. The method of grouping together atoms that are bonded to the same atom to give a **condensed structure,** which was presented in Chapter 1, can be used, but even this becomes tedious. *An even faster method, called a* ***skeletal structure,*** *shows the C—C bonds as lines.* Each line is assumed to have a C at each end unless another atom is shown. Hydrogens on the C's are not shown. (However, if a carbon is shown with a C, the hydrogens on it must also be shown as H's.) All other atoms (N, O, Cl, and so on) must be shown, along with any hydrogens bonded to them. Unshared pairs of electrons may or may not be shown. Sometimes the various methods are mixed to emphasize a particular feature. Figure 2.5 shows four of the possible isomers of $C_5H_{10}O$ using these various methods.

Important Convention

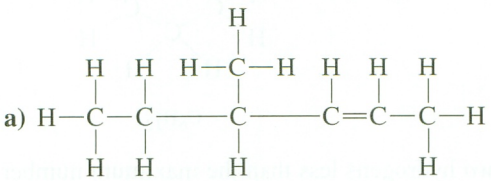
PROBLEM 2.5

Calculate the DU for these formulas and draw two constitutional isomers for each:

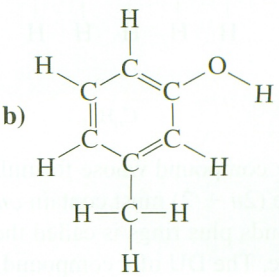
a) $C_{10}H_{22}$ **b)** C_9H_{16} **c)** C_6H_6

PROBLEM 2.6

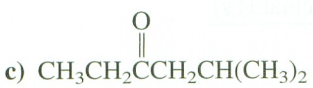
Convert these structures to skeletal structures:



a)

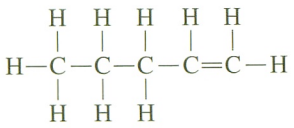
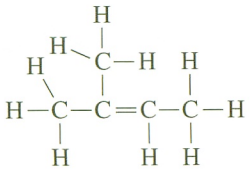
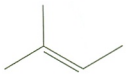
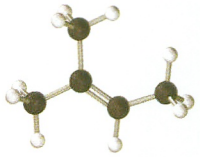
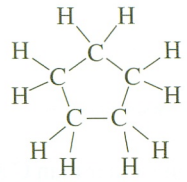
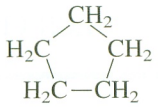
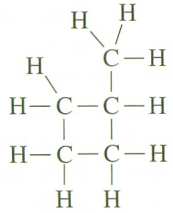
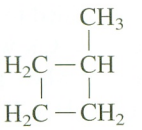
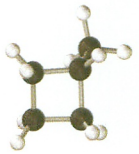


b)



c) $CH_3CH_2CCH_2CH(CH_3)_2$

d) $CH_3CHCH_2NHCH_2CH_2CH_3$

Line structure or Kekulé structure	Condensed structure	Skeletal structure	Molecular model
	$CH_3CH_2CH_2CH{=}CH_2$		
	CH_3 $CH_3C{=}CHCH_3$ or $(CH_3)_2C{=}CHCH_3$		
			
			

ⓐ This represents a C bonded to one other C (at the other end of the line). It must be bonded to three H's to complete its valence.

ⓑ This represents a C bonded to two other C's. It is also bonded to two H's that are not shown.

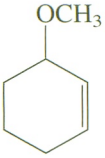
ⓒ This represents a C double bonded to another C. It is also bonded to two H's that are not shown.

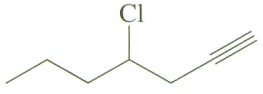
Figure 2.5

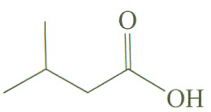
LINE, CONDENSED, AND SKELETAL STRUCTURES AND MOLECULAR MODELS FOR SOME ISOMERS OF C_5H_{10}.

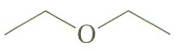
PROBLEM 2.7

Convert these skeletal structures to line structures:

a) 

b) 

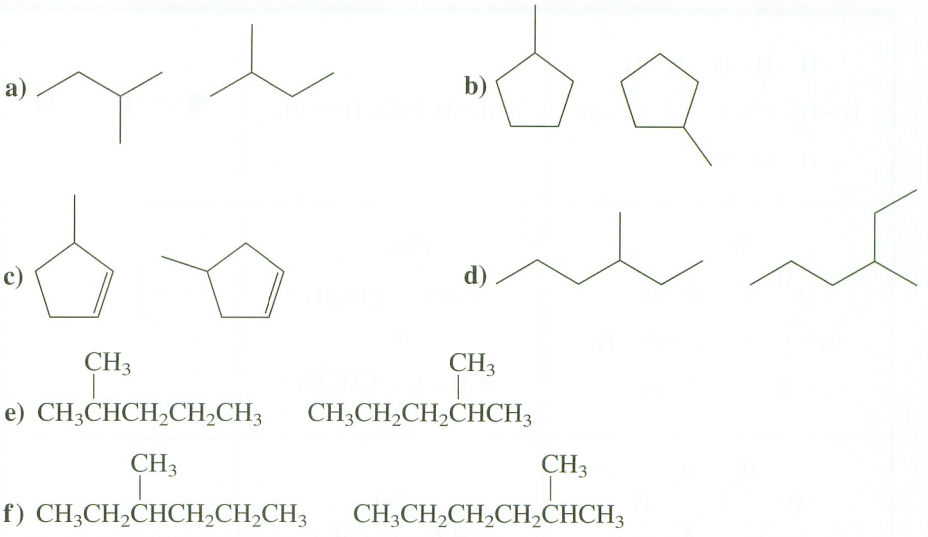
c) 

d) 

ORGANIC Chemistry Now™
Click *Coached Tutorial Problems* to practice **Drawing Skeletal Structures** and **Recognizing Isomerism.**

PROBLEM 2.8

Determine whether these structures represent the same compound or isomers:

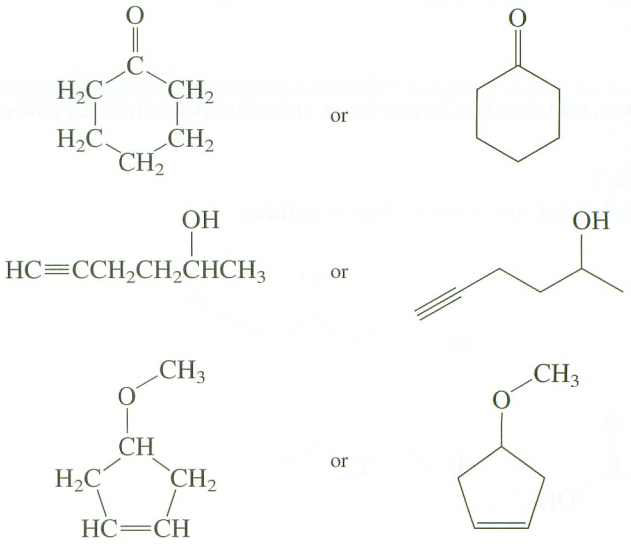


The DU can also be calculated for formulas that have atoms other than C and H. Because halogens are monovalent, they are counted as hydrogens in the DU calculation. For example, $C_5H_{11}Cl$ is counted as C_5H_{12} and has DU = 0—it is saturated.

Oxygen is divalent. If an O is added to a structure, it can, for example, be inserted between a C and H or between two C's without changing the number of hydrogens. Therefore, we can ignore oxygens when performing a DU calculation. The DU for $C_6H_{10}O$ is 2, the same as that for C_6H_{10}. This compound must have two double bonds, one triple bond (a triple bond contributes 2 to the DU), one double bond and one ring, or two rings. Although the presence of oxygen is ignored in calculating the DU, oxygen can, of course, be involved in the features, double bonds or rings, that contribute to the DU. Figure 2.6 shows several isomers for $C_6H_{10}O$.

Figure 2.6

THREE (OF MANY) CONSTITUTIONAL ISOMERS OF $C_6H_{10}O$.



Finally, let's consider the effect of nitrogen on a DU calculation. Nitrogen is trivalent. If an N is added to a structure by inserting it between two atoms, one H must also be added to satisfy the third valence of the N. Therefore, each nitrogen that is present in a compound increases the maximum number of H's by one. For example, the maximum number of H's for $C_{10}H_{15}N$ is $2(10) + 2 + 1 = 23$. The DU is $(23 - 15)/2 = 4$.

You must be very careful when using a shorthand method to show structures. Beginning organic chemistry students commonly forget about hydrogens or do not recognize other features of such structures. *It is often a good idea to redraw the structures more completely, showing each carbon and all the hydrogens, until you are very comfortable with them and can automatically picture all the features of the molecule.*

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Click *Coached Tutorial Problems* to practice **Determining Degrees of Unsaturation.**

PRACTICE PROBLEM 2.2

Calculate the DU for $C_8H_{13}BrO$.

Solution

Br counts as an H and O can be ignored, so calculate as though the formula were C_8H_{14}. DU $= \frac{1}{2}[(2)(8) + 2 - 14] = 2$.

PROBLEM 2.9

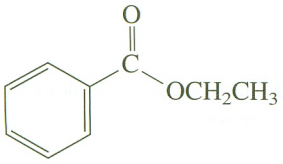
Calculate the DU for these formulas and draw two constitutional isomers for each:

a) $C_{10}H_{20}O$ **b)** C_6H_9N **c)** $C_7H_{14}F_2$
d) C_6H_8ClN **e)** $C_9H_{15}NO$

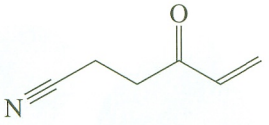
PROBLEM 2.10

Determine the DU for each of these structures:

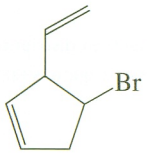
a)



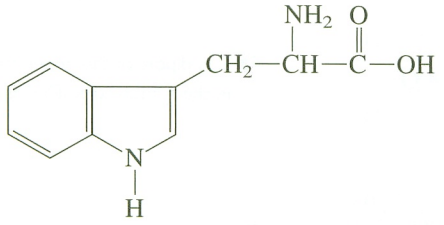
b)



c)

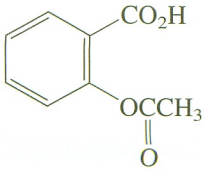


d)



Tryptophan (an amino acid)

e)



Acetylsalicylic acid (aspirin)

BioLink

2.5 Physical Properties and Molecular Structure

The **physical properties** of a compound are properties such as its melting point, boiling point, or solubility in a particular solvent. These properties all depend on the strength of the attractions between the molecules. The intermolecular attractive forces result from a charge or partial charge on one molecule interacting with a charge or partial charge on another molecule. The attraction between a positive and a negative center becomes stronger as the magnitude of the charges increases and as the distance between them decreases. The various types of charge–charge interactions that are important are shown in Figure 2.7.

Ion–ion interactions are the strongest of these because they involve the most charge. For example, the strength of the forces holding sodium and chloride ions to-

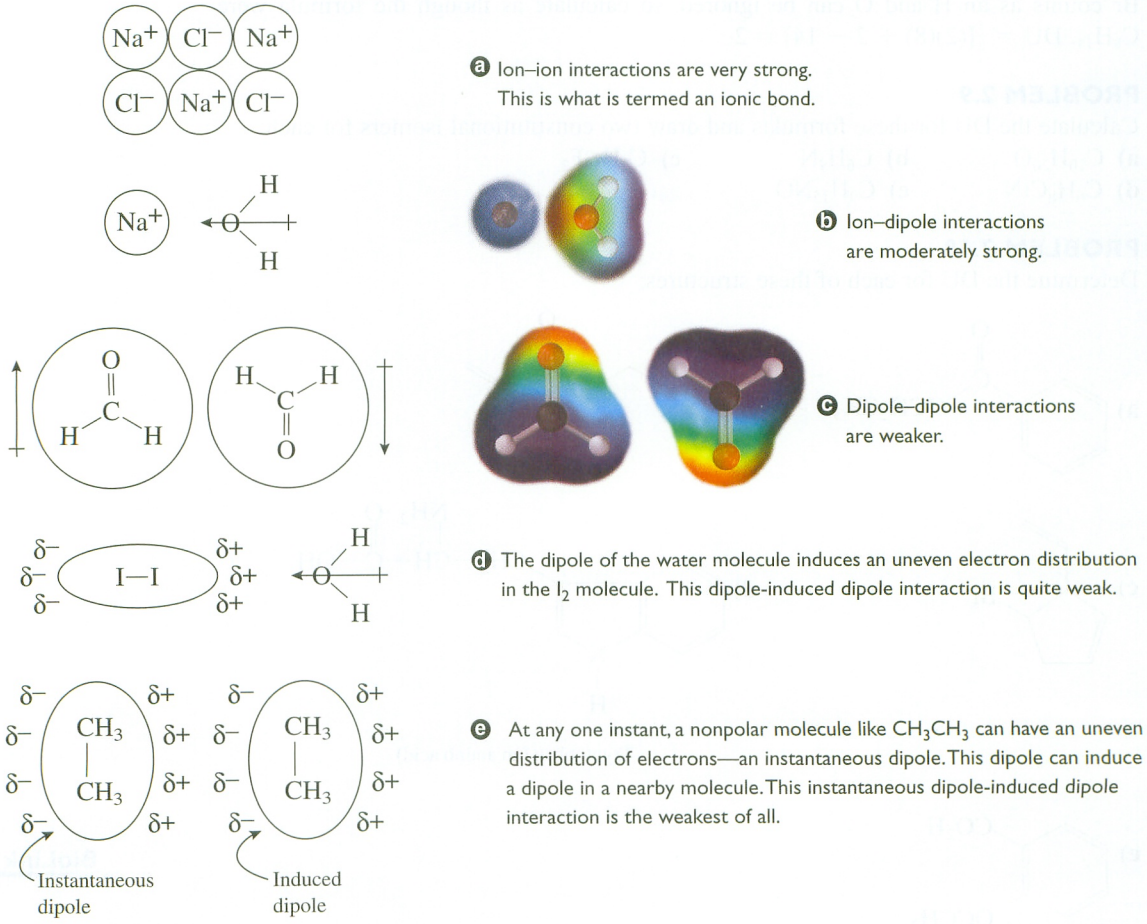
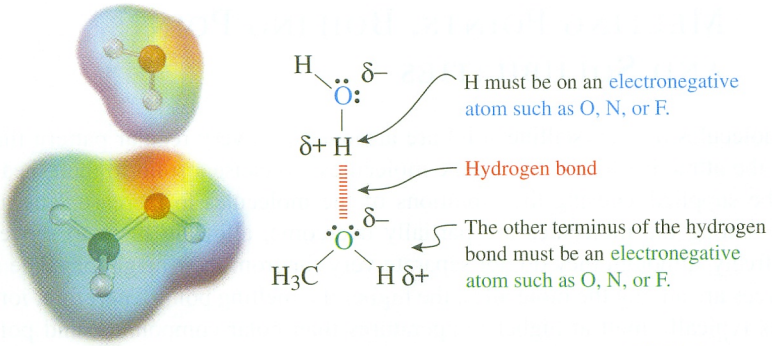

Na+ Cl− Na+
Cl− Na+ Cl−
Na+
H
O
H
O
H H
C
H H
C
O
δ− δ+
I—I
H
O
H
CH3
CH3
Instantaneous dipole
Induced dipole
a Ion–ion interactions are very strong. This is what is termed an ionic bond.
b Ion–dipole interactions are moderately strong.
c Dipole–dipole interactions are weaker.
d The dipole of the water molecule induces an uneven electron distribution in the I2 molecule. This dipole-induced dipole interaction is quite weak.
e At any one instant, a nonpolar molecule like CH3CH3 can have an uneven distribution of electrons—an instantaneous dipole. This dipole can induce a dipole in a nearby molecule. This instantaneous dipole-induced dipole interaction is the weakest of all.

Figure 2.7

TYPES OF CHARGE–CHARGE INTERACTIONS.


H must be on an electronegative atom such as O, N, or F.
Hydrogen bond
The other terminus of the hydrogen bond must be an electronegative atom such as O, N, or F.

Active Figure 2.8 ORGANIC Chemistry Now™

AN EXAMPLE OF HYDROGEN BONDING. Test yourself on the concepts in this figure at **OrganicChemistryNow.**

gether in the crystal lattice is 188 kcal/mol (788 kJ/mol). (Compare this to a typical covalent bond strength of about 100 kcal/mol [418 kJ/mol].) Because a large amount of heat energy must be added to disrupt these forces, ionic compounds typically have high melting and boiling points. For example, NaCl melts at 801°C, whereas CH_3Cl melts at −98°C.

Because of the lesser amount of charge involved when an ion interacts with a polar molecule, the magnitude of the resulting **ion–dipole** attraction is much less than that of an ion–ion attraction. The strength of the attraction continues to decrease as the amount of charge decreases. Therefore, the attraction of polar molecules for each other (**dipole–dipole**) is weaker than that of an ion for a polar molecule. The force attracting a polar molecule to a nonpolar molecule (**dipole-induced dipole**) is still weaker. The attraction between nonpolar molecules (**instantaneous dipole-induced dipole** or **London force**) is the weakest of all, but the total London force in a large molecule can be reasonably large and can have an important effect on the physical properties of the compound. These last three interactions are often called **van der Waals forces** and range from approximately 5 to 0.5 kcal/mol (20–2 kJ/mol).

Another very important type of charge–charge interaction is **hydrogen bonding.** This interaction, illustrated in Figure 2.8, is a special type of dipole–dipole attraction. In hydrogen bonding, a hydrogen on an electronegative atom (O, N, or F) is the positive part of a dipole and is attracted to the negative end of a dipole (O, N, or F) in another molecule. Because of the small size of hydrogen, the partial charges are able to approach more closely, and a stronger than usual attraction—a hydrogen bond—results. The strength of a hydrogen bond is commonly in the range of 3 to 8 kcal/mol (12–34 kJ/mol). Because C—H bonds are not very polar, these H's do not usually hydrogen bond to any appreciable extent.

PROBLEM 2.11

What kinds of attractive intermolecular forces are found in each of these compounds?

a) $CH_3CH_2CH_3$ **b)** CH_3OCH_3 **c)** $CaCl_2$ **d)** CH_3OH

PROBLEM 2.12

Show the hydrogen bond that is present in liquid ammonia, $NH_3(l)$.

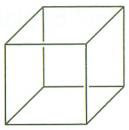
2.6 Melting Points, Boiling Points, and Solubilities

The molecules of a crystalline solid are arranged in a very regular pattern that maximizes the attractive forces among the molecules. To cause a solid to melt, heat energy must be supplied, causing the vibrations of the molecules to increase. The attractive forces among the molecules are partially overcome, allowing them to move around more freely, although they do not separate very far from their neighbors. The stronger the forces are among the molecules, the higher the melting point. Therefore, ionic compounds typically melt at higher temperatures than polar compounds, and polar compounds melt at higher temperatures than nonpolar compounds. The melting points of both polar and nonpolar compounds increase as their molecular masses increase because the larger molecules have more London forces between them. Finally, the shape of a compound is very important and has a dramatic effect on its melting point. More symmetrical molecules pack into the crystal lattice better, allowing closer approach and larger attractive forces, resulting in higher melting points. Some examples of these effects are shown in Table 2.4.

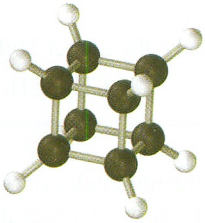
The compound known as cubane, one of the isomers of the formula C_8H_8, has its eight carbons arranged at the vertices of a cube. It is the ultimate example of the effect of shape on melting point. Octane, a straight-chain saturated hydrocarbon with the formula C_8H_{18}, has a melting point of −57°C. Because of its symmetrical shape, cubane packs much better into the crystal lattice. The melting point of cubane is 131°C.

Table 2.4 Examples of the Dependence of Melting Points on Structure

Compound	Melting Point (°C)	Comment
NaCl	801°	Ionic compounds have high melting points.
LiF	842°	Smaller ions are closer together.
$CH_3CH_2CH_3$	−190°	Small (low molecular mass) nonpolar compounds have low melting points.
$CH_3CH_2CH_2CH_2CH_3$ Pentane	−130°	Melting points increase with increasing molecular mass.
$CH_3C(CH_3)_2CH_3$ 2,2-Dimethylpropane	−71°	This isomer of pentane has a more compact spherical shape, which allows it to pack better into the crystal lattice, resulting in a significantly higher melting point.
$CH_3CH_2CH_2C(=O)H$ Butanal	−99°	Butanal has the same molecular mass and same general shape as pentane. It is higher melting than pentane because the dipole–dipole forces of the polar C=O group hold the molecules together more strongly.



Cubane
mp = 131°C



$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Octane
mp = −57°C

PROBLEM 2.13

Explain whether you would expect KBr or CH_3Br to have the higher melting point.

In the liquid phase, molecules are free to move about, although they are always close to other molecules and interacting with them. To cause a molecule to enter the vapor phase, enough energy must be added to entirely overcome the forces attracting it to other molecules. Therefore, as is the case with melting points, boiling points increase as the forces between the molecules become stronger. However, the effect of the shape of the molecule on its boiling point is quite different from the effect on its melting point. Because liquids have little order, symmetrical compounds do not have higher boiling points. In fact, longer, rod-shaped molecules have more surface area than do spherical molecules of similar molecular mass, so such rod-shaped molecules have slightly higher boiling points owing to increased London forces. In addition, the presence of hydrogen bonding increases boiling points much more than melting points. Some examples of these effects are shown in Table 2.5.

Table 2.5 Examples of the Dependence of Boiling Points on Structure

Compound	Normal Boiling Point (°C)	Comment
NaCl	1413°	Ionic compounds have high boiling points.
LiF	1676°	Smaller ions are closer together.
$CH_3CH_2CH_3$	−42°	Small nonpolar compounds have low boiling points.
$CH_3CH_2CH_2CH_2CH_3$ Pentane	36°	Boiling points increase with increasing molecular mass.
$CH_3C(CH_3)_2CH_3$ 2,2-Dimethylpropane	10°	Although this isomer is more symmetrical and has a higher melting point, the rod shape of pentane has more surface area, resulting in a higher boiling point due to increased London forces.
$CH_3CH_2CH_2CHO$ Butanal	76°	Butanal has the same molecular mass as pentane. It is higher boiling than pentane because of the polar C=O group.
$CH_3CH_2CH_2CH_2OH$ *1-Butanol*	117°	1-Butanol boils significantly higher than the compound above because its molecules can hydrogen bond to each other.

PROBLEM 2.14

Which of these isomers would you expect to have the higher boiling point? Explain.

$CH_3CH_2CH_2OH$ or $CH_3CH_2OCH_3$

When a compound dissolves in a solvent, the molecules of that compound become separated. These molecules then mix among the solvent molecules, separating the latter molecules also. Therefore, energy must be supplied to overcome both the forces holding the solute molecules together and the forces holding the solvent molecules together. Some energy is returned from the interactions between solute and solvent molecules. Usually, the total amount of energy that must be added to overcome the attractive forces among the solute molecules and the attractive forces among the solvent molecules is somewhat greater than the amount of energy that is released by the interactions of the solute with the solvent molecules. Overall, energy must be added to the system—that is, the process is **endothermic:** the enthalpy change is positive ($\Delta H > 0$).

Why, then, does a solution ever form? You may recall from general chemistry that whether a reaction is spontaneous or not depends on both the enthalpy and the entropy of that process. **Entropy** (S) is a measure of disorder. Processes that increase the disorder in a system ($\Delta S > 0$) are favored. Although most solution processes are endothermic (disfavored by enthalpy, $\Delta H > 0$), the solution is more disordered than the separate solute and solvent (favored by entropy, $\Delta S > 0$). Therefore, as long as the process is not too endothermic, the favorable entropy change will cause the solute to dissolve. Whether the process is likely to be too endothermic can be estimated by examining the

Focus On

Boiling Points of Fuels

Charles D. Winters

Some camping stoves use butane as a fuel.

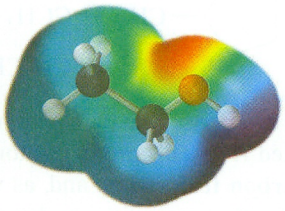
The hydrocarbons methane, propane, and butane are all used as fuels in various applications. The boiling points of these compounds increase with increasing molecular mass and help determine the use for each fuel. Methane has a boiling point of −162°C and is the major component of natural gas. Because of its low boiling point, it is difficult to liquefy. Propane boils at −42°C and is more easily liquefied than natural gas; that is, it is a liquid at lower pressures than natural gas. Pressurized tanks containing liquid propane are used as fuel sources for home heating in areas that are not served by natural gas pipelines and for such uses as portable barbecue grills. Butane boils at −0.5°C and is a liquid at pressures only slightly above 1 atmosphere. Plastic containers of liquid butane are used in cigarette lighters. These lighters do not work well if they are allowed to become very cold because then the butane will not vaporize.

CH_4	$CH_3CH_2CH_3$	$CH_3CH_2CH_2CH_3$
Methane	Propane	Butane
bp = −162°C	bp = −42°C	bp = −0.5°C

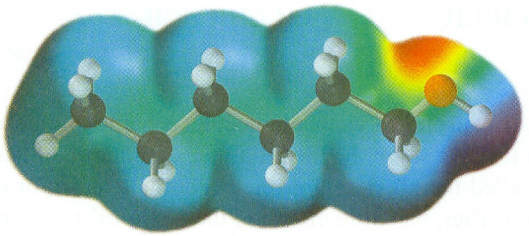
solute and the solvent. If either the attractive force between solute molecules or that between solvent molecules is considerably larger than the attractive force between a solute and a solvent molecule, the process will be too endothermic and the solution will not form. In other words, the new interactions in the solution must be comparable in strength to the old interactions in the solute and in the solvent. This means that the solute and the solvent must be similar so that the forces between them are similar in magnitude to the forces just in the solute or in the solvent. A common way of stating this is "like dissolves like," which simply means that the polarities of the solute and the solvent must be similar.

Sodium chloride dissolves in water, a very polar solvent. Although the interactions between the water molecules and the sodium and chloride ions are not as strong as the interactions between the ions themselves, they are potent enough to make the process only somewhat endothermic. Entropy then makes the overall process favorable. Sodium chloride does not dissolve in a nonpolar solvent such as pentane ($CH_3CH_2CH_2CH_2CH_3$) because the interactions between the pentane molecules and the ions are too weak in comparison to the forces between the ions, making the overall process too endothermic for entropy to overcome.

If pentane and water are mixed, they form separate layers—they do not dissolve—because the attractive forces between pentane and water molecules are much smaller than the forces between water molecules. Pentane is termed a **hydrophobic** (water-hating) compound. Ethanol, CH_3CH_2OH, has a nonpolar, hydrophobic part (the CH_3CH_2) and a polar, **hydrophilic** (water-loving) part (the OH). The effects of the two parts are in competition, but in this case the hydrophilic part wins, and ethanol is **miscible** (mixes in all proportions) with water. As we might expect, as the hydrophobic part of the molecule becomes larger, the compound becomes less water soluble. Thus, butanol, $CH_3CH_2CH_2CH_2OH$, is only slightly soluble in water (7.4 g/100 mL), and hexanol, $CH_3CH_2CH_2CH_2CH_2CH_2OH$, is even less soluble (0.6 g/100 mL). Many organic compounds have a large hydrophobic part and are essentially insoluble in water. However, they are often soluble in less polar solvents such as ethanol, diethyl ether ($CH_3CH_2OCH_2CH_3$), and dichloromethane (CH_2Cl_2).



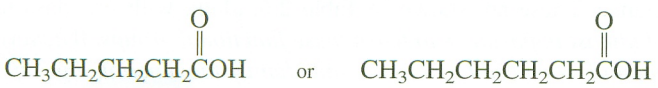
Ethanol, CH_3CH_2OH



Hexanol, $CH_3CH_2CH_2CH_2CH_2CH_2OH$

PROBLEM 2.15

Which of these compounds would you expect to be more soluble in water? Explain.

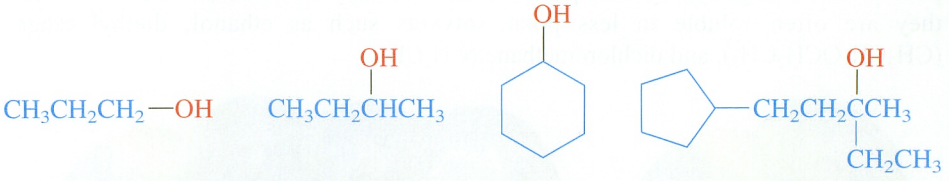


2.7 Introduction to Functional Groups

As we have seen, the number of possible organic compounds is virtually limitless. How can anyone learn the chemistry of all of them? Fortunately, we do not need to learn an entire new set of chemical reactions for each new compound encountered. A particular arrangement or group of atoms has very similar chemistry no matter what the remainder of the molecule looks like.

Let's consider the two compounds $CH_3CH_2CH_2OH$ and $CH_3CH_2CH_2CH_2OH$. They are quite similar, and on the basis of the material presented in Section 2.6, they should have similar physical properties. The polarity and hydrogen bonding of the OH group cause both of them to have higher boiling points than similar compounds containing only C and H. Because the second one has a greater molecular mass, it is expected to have a somewhat higher boiling point. The OH group should also confer a degree of water solubility on each. Because the second has a larger nonpolar part, it should be less water soluble than the first. Indeed, these expectations are borne out. It is probably not surprising to discover that these two compounds also undergo very similar chemical reactions. So if we learn the reactions of one, we will know much about the reactions of the other.

As we learn more about organic chemistry, we will find that the attraction between positive and negative charges, or partial charges, is instrumental in many chemical reactions. Often a reaction begins by the reagent being attracted to the polar part of a molecule. Therefore, the reactions of the molecules on the previous page occur at the polar sites: the O—H and C—O bonds. The C—C single bonds and the C—H bonds are not very reactive. In fact, in terms of chemical reactions, it makes little difference how many C—C or C—H bonds the molecule has or exactly how they are arranged. The reactions occur at the OH group. Thus, all of the following compounds exhibit very similar chemical behavior!

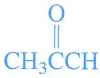
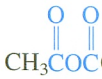
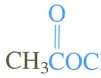


It is useful to view a molecule as being composed of two parts. One part only has C's that are singly bonded to other C's (and their associated H's). This group of atoms is called the **alkyl group,** the **carbon skeleton,** or the **carbon framework** and, as we saw earlier, has little effect on the chemical reactions. The other part of the molecule, where the action is, is called the **functional group.** All of the preceding compounds have the same functional group, the OH group, but different alkyl groups. The class of compounds with the OH functional group is called alcohols. *A general alkyl group is represented by R, so all alcohols can be depicted as ROH.* All alcohols have similar chemical reactions.

Important Convention

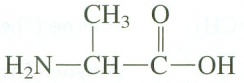
The concept of functional groups is a very powerful organizing feature for organic chemistry. All compounds with the same functional group have very similar reactions, regardless of their carbon skeleton. Only a limited number of functional groups are of major importance. These are shown in Table 2.6, along with the class name of each group. *It is of utmost importance to learn these functional groups. Whenever you see an organic compound, you need to focus on and identify the functional group because that*

Table 2.6 Common Functional Groups

General Formula	Example	Name
RH	$CH_3CH_2CH_3$	**Alkane** (Alkanes have no functional group.)
$RCH{=}CH_2$	$CH_3CH_2CH{=}CH_2$	**Alkene** (The functional group is the carbon–carbon double bond.)
$RC{\equiv}CH$	$CH_3C{\equiv}CH$	**Alkyne** (The functional group is the carbon–carbon triple bond.)
ArH		**Arene** (A six-membered ring with three double bonds has different reactions than an alkene so it is given a different name. Arenes or **aromatic rings** can have alkyl or other groups attached to the ring.)
RX	$CH_3CH_2CH_2Cl$	**Alkyl halide** (The functional group is the carbon–halogen bond.)
ROH	CH_3CH_2OH	**Alcohol** (The functional group is the C—O—H.)
ROR	$CH_3CH_2OCH_3$	**Ether** (The functional group is the C—O—C. The alkyl groups on the O can be the same or different.)
RNH_2	$CH_3CH_2CH_2NH_2$	**Amine** (The C—N is the functional group. The other H's on the N can be replaced with alkyl groups.)
		Aldehyde (The functional group is the C=O with at least one H on the C.)
		**Ketone** (The functional group is the C=O with two alkyl groups on the C. The alkyl groups need not be the same.)
		Carboxylic acid (The functional group is the .)
		Acyl chloride (The functional group is the .)
		**Acid anhydride** (The functional group is the . The alkyl groups may be different.)
		**Ester** (The functional group is the .)
		Amide (The functional group is the . The other groups on the N may be H's or alkyl groups.)
$RC{\equiv}N$	$CH_3CH_2CH_2C{\equiv}N$	**Nitrile** (The functional group is the carbon–nitrogen triple bond.)

is where the reactions will occur—where the action is. And if you know the reactions of that functional group, you will know much about the reactions of that compound.

More complex compounds can have more than one functional group. For example, alanine, an important amino acid in nature, has both an amine and a carboxylic acid functional group.



Alanine
(an amino acid)

In the next chapter we will reexamine bonding, using orbitals. This will provide a better picture of why some bonds are stable and others are not.

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Click *Coached Tutorial Problems* for more practice in **Identifying Functional Groups**.

PROBLEM 2.16

Which functional group is present in each of these compounds?

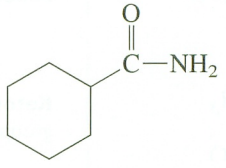
a) $CH_3CH_2CH_2CH_2OCH_3$

b)

c) $CH_3CH_2CH_2CO_2H$

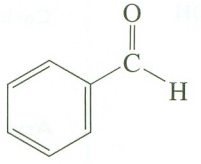
Careful: how are the O's bonded to the C?

d)



e) CH_3COCH_3

f)



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Click *Mastery Goal Quiz* to test how well you have met these goals.

Review of Mastery Goals

After completing this chapter, you should be able to:

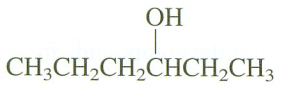
- Quickly recognize the common ways in which atoms are bonded in organic compounds. You should also recognize unusual bonding situations and be able to estimate the stability of molecules with such bonds.
- Know the trends in bond strengths and bond lengths for the common bonds. (Problem 2.37)
- Recognize when compounds are constitutional isomers and be able to draw constitutional isomers for any formula. (Problems 2.21, 2.22, 2.23, 2.24, 2.39, and 2.40)
- Calculate the degree of unsaturation for a formula and use it to help draw structures for that formula. (Problems 2.25, 2.26, 2.40, 2.45, and 2.46)

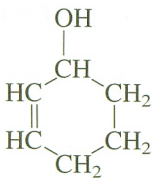
- Draw structures using any of the methods we have seen. You should also be able to examine a shorthand representation for a molecule and recognize all of its features. (Problems 2.17 and 2.18)
- Examine the structure of a compound and determine the various types of intermolecular forces that are operating. You should be able to crudely estimate the physical properties of the compound. (Problems 2.27, 2.28, 2.29, 2.30, 2.31, 2.32, 2.33, 2.34, 2.35, 2.36, 2.43, and 2.44)
- Recognize and name all of the important functional groups. (Problems 2.19, 2.20, 2.42, 2.43, and 2.46)

Additional Problems

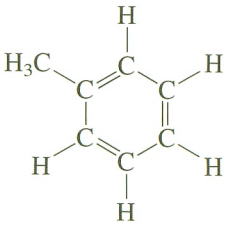
ORGANIC Chemistry Now™
Assess your understanding of this chapter's topics with additional quizzing and conceptual-based problems at **http://now.brookscole.com/hornback2**

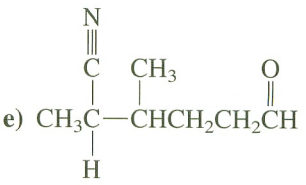
2.17 Convert the following structures to skeletal structures:

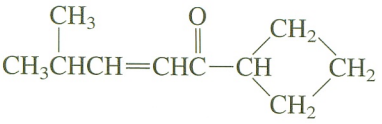
a) 

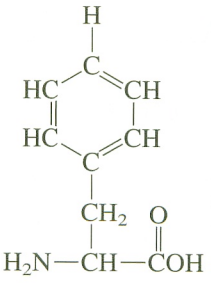
b) 

c)

d) 

e) 

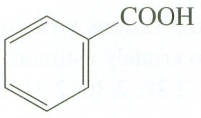
f) 

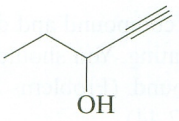
g) 

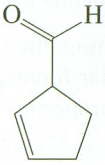
Phenylalanine
(an amino acid)

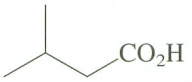
BioLink

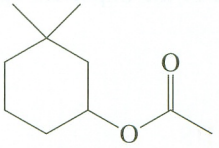
2.18 Convert the following shorthand representations to structures showing all of the atoms, bonds, and unshared electron pairs:

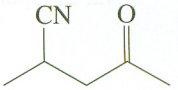
a) 

b) 

c) 

d) 

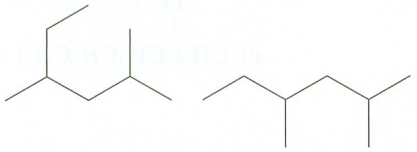
e) 

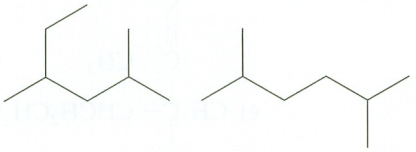
f) 

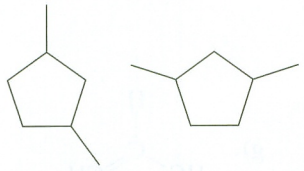
2.19 Name the functional group(s) present in each of the compounds in problem 2.17.

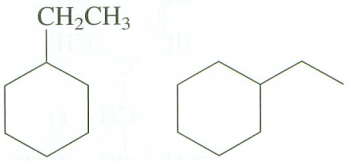
2.20 Name the functional group(s) present in each of the compounds in problem 2.18.

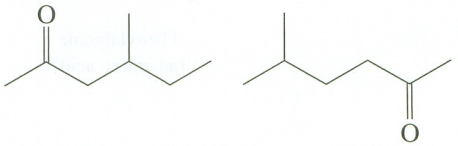
2.21 Determine whether these structures represent the same compound or isomers:

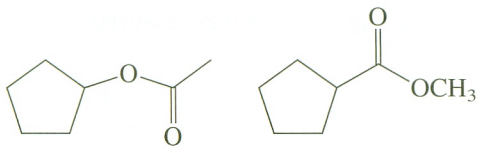
a) 

b) 

c) 

d) 

e) 

f) 

2.22 Draw all the isomers for each of these formulas. The total number for each is given in parentheses.

a) C_3H_8O (3) **b)** C_4H_9Cl (4) **c)** C_4H_8 (5)
d) C_7H_{16} (9)

2.23 The formula C_4H_8O has many isomers.

a) Draw three isomers that have a carbon–oxygen double bond. What functional group is present in each of them?
b) Draw three alcohols with this formula.
c) Draw an ether with this formula that does not have a carbon–carbon double bond.

2.24 Four of the ten isomers of C_5H_{10} are shown in Figure 2.5. Draw four other isomers with this formula.

2.25 Calculate the DU for each of these formulas and draw a structure that meets the listed restriction:

a) C_5H_9NO (not an amine)
b) $C_7H_{12}O$ (a ketone)
c) $C_6H_{14}O$ (does not hydrogen bond)
d) C_7H_8 (an aromatic compound)

2.26 Can $C_8H_{17}N$ have a nitrile as its functional group? Explain.

2.27 Show all the different hydrogen bonds that would occur in a mixture of

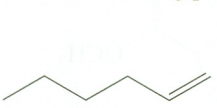
a) CH_3CH_2OH and H_2O
b) CH_3OH and

2.28 One of these isomeric alcohols has mp = 26°C and bp = 82°C; the other has mp = −90°C and bp = 117°C. Explain which isomer has the higher melting point and which has the higher boiling point.

2.29 Explain the differences in the boiling points between the members of each of these pairs of compounds:

a) $CH_3(CH_2)_6CH_3$ bp: 126°C
$CH_3(CH_2)_8CH_3$ bp: 174°C
b) $CH_3CH_2CH_2OH$ bp: 97°C
$CH_3CH_2OCH_3$ bp: 11°C
c) $CH_3CH_2CH_3$ bp: −42°C
CH_3OCH_3 bp: −23°C

2.30 Explain the difference in the melting points of these isomers:



mp = −140°C

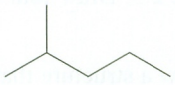
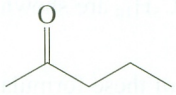
mp = 7°C

2.31 Explain which compound you expect to have the higher melting point.

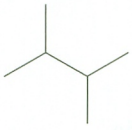
a) or

b) $CH_3(CH_2)_{18}CH_3$ or $CH_3(CH_2)_{29}CH_3$

Beeswax

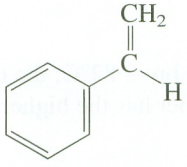
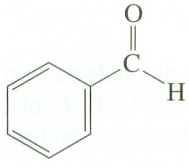
c)  or 

2.32 Explain which compound you expect to have the higher boiling point.

a)  or

b) $CH_3CH_2\overset{O}{\overset{\|}{C}}OH$ or $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H$

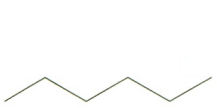
c) $CH_3CH_2OCH_2CH_3$ or $CH_3CH_2CH_2OCH_2CH_2CH_3$

d)  or 

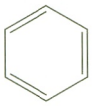
2.33 Which of these two salts would you expect to be more soluble in hexane (C_6H_{14})?

$\overset{+}{N}H_4\ \overset{-}{Cl}$ or $\overset{+}{N}(CH_2CH_2CH_2CH_3)_4\ \overset{-}{Cl}$

2.34 Benzene and hexane are both liquids at room temperature. Do you expect benzene and hexane to be miscible? Do you expect benzene and water to be miscible? Explain.



Hexane

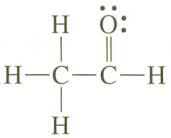


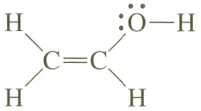
Benzene

2.35 One of these isomers is miscible with water, and the other is nearly insoluble. Explain.

2.36 Because of two hydrogen bonds, carboxylic acids show a very strong attractive force between two molecules that persists even in the gas phase. Show this hydrogen bonding between two carboxylic acid molecules.

2.37 Bond strengths can be used to estimate the relative stability of isomers that have different bonds. The isomer that has the larger total bond energy is more stable. One of the following isomers is more stable than the other. The less stable one is rapidly converted to the more stable one, so it cannot be isolated. On the basis of bond dissociation energies, which of these two isomers is more stable?





2.38 Bond strengths can also be used to estimate whether a reaction is energetically favorable or not—that is, whether the reactants or the products are more stable. Use bond dissociation energies to determine whether this reaction is energetically favorable. The bond dissociation energy for H_2 is 104 kcal/mol (435 kJ/mol).

2.39 One of the isomers of C_5H_{12} reacts with Cl_2 in the presence of light to produce three isomers of $C_5H_{11}Cl$:

One isomer Three isomers

This reaction replaces *any one* of the hydrogens of C_5H_{12} with a Cl. What are the structures of the C_5H_{12} isomer and the three $C_5H_{11}Cl$ isomers produced from it?

2.40 On reaction with Cl_2 in the presence of light, an unknown compound with the formula C_5H_{10} gives only one isomer of C_5H_9Cl (see problem 2.39). What is the DU of the unknown compound? Show the structure of the unknown compound and the product of its reaction with Cl_2.

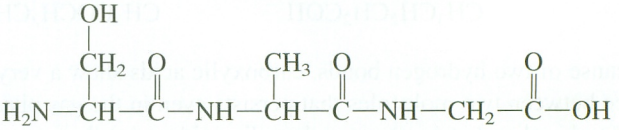
$$C_5H_{10} + Cl_2 \xrightarrow{\text{light}} C_5H_9Cl + H{-}Cl$$

One isomer

2.41 Explain how the dipole moment for CH_3Cl ($\mu = 1.9$ D) can be larger than the dipole moment for CH_3F ($\mu = 1.8$ D).

BioLink

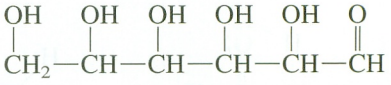
2.42 Peptides are smaller versions of proteins and have similar functional groups. What functional groups are present in this peptide?



Serine-alanine-glycine

BioLink

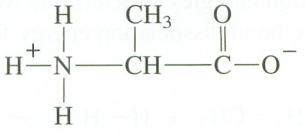
2.43 Glucose is a typical carbohydrate. What functional groups are present in glucose? What would you predict about the water solubility of glucose? Offer a reason why nature uses carbohydrates rather than alkanes as an energy source.



Glucose

BioLink

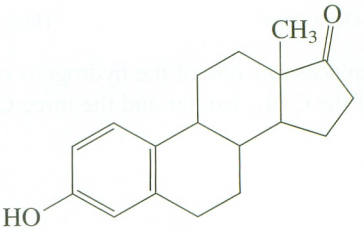
2.44 Amino acids such as alanine actually exist as species called zwitterions, with a positive charge on the nitrogen and a negative charge on the oxygen. Explain what effect you expect this to have on the melting point of alanine.



Alanine zwitterion

BioLink

2.45 What is the DU of estrone, a female sex hormone? Use the number of carbons and oxygens in estrone to calculate the number of hydrogens it has.

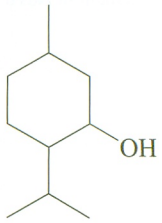


Estrone

2.46 What functional groups are present in these molecules? What is the DU of each?

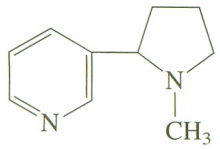
BioLink

a)



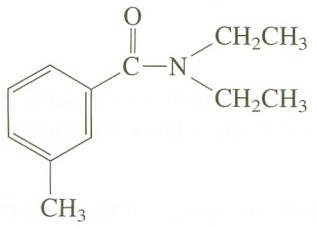
Menthol
(an ingredient of peppermint oil)

b)



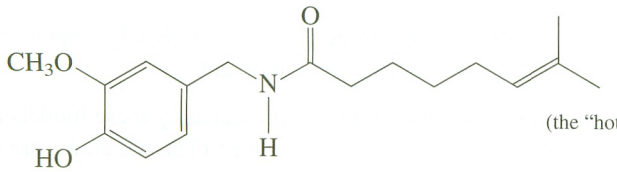
Nicotine
(the addictive substance in tobacco)

c)



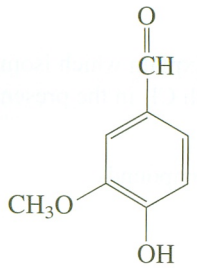
N,N-Diethyl-*m*-toluamide
(DEET, a mosquito repellant)

d)



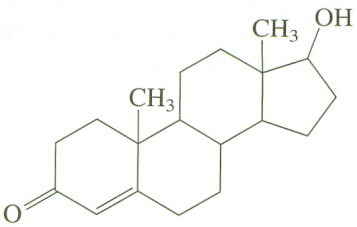
Capsaicin
(the "hot" ingredient in chili peppers)

e)

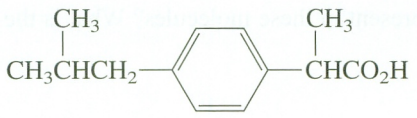


Vanillin
(major component of vanilla flavoring)

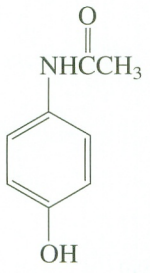
f)



Testosterone
(a male sex hormone)

g) 

Ibuprofen
(active ingredient in Advil and Motrin)

h) 

Acetaminophen
(active ingredient in Tylenol)

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2.47 Explain whether each pair of models represent isomers or the same compound. (All represent compounds with the formula C_7H_{16}.) Draw structures for each compound represented by the models.

2.48 Explain whether each pair of models represent isomers or the same compound. Draw structures for each compound represented by the models.

2.49 The following models represent three isomers of $C_6H_4Cl_2$. Explain which of these compounds does not have a dipole moment.

2.50 Draw the structures of the compounds represented by these models and explain which would have the larger solubility in water. (The red atoms are oxygens.)

2.51 Draw the structures of the compounds represented by these models and explain which would have the higher melting point.

2.52 These models show the three isomers of C_5H_{12}. Explain which isomer would produce only one $C_5H_{11}Cl$ isomer on reaction with Cl_2 in the presence of light. (See problem 2.39.)

2.53 Determine the degree of unsaturation for these compounds.

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